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Bimetallic complexes III [1]. Synthesis and reactions of $C_5H_4PPh_2$-bridged zirconium–molybdenum and zirconium–tungsten complexes [2]

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Abstract

The synthesis and reactions of bimetallic Zr–Mo and Zr–W complexes with bridging $C_5H_4PPh_2$ ligands (henceforth abbreviated as Cp′) are described. Reaction of Cp'_2ZrCl_2 (**1**) with organolithium or Grignard reagents gives Cp'_2ZrR_2 (R = Me (**3**), p-$C_6H_4CH_3$ (**5**), CH_2SiMe_3 (**6**)) while with $AlMe_3$ the mono-exchange product $Cp'_2Zr(Cl)Me$ (**2**) is formed. Phenyllithium converts **2** into $Cp'_2Zr(Me)Ph$ (**4**). From **1–3** the substitution products $[(Cp'_2ZrMe)_2(\mu\text{-}O)]$ (**7**), $Cp'_2Zr(SR)_2$ (R = Me (**8a**), Ph (**8b**), $CH_2C_6H_4Cl$ (**8c**)), $Cp'_2Zr(Me)OR$ (R = CH_2CF_3 (**9a**), *t*-Bu (**9b**)), and $Cp'_2Zr(Cl)O$*t*-Bu (**10**) were obtained. Treatment of $[Mo(CO)_4(norbornadiene)]$ with either **2**, **4** or **9a** gives the bis-Cp′ bridged binuclear tetracarbonyl complexes $[Cp'_2Zr(Me)(X)Mo(CO)_4]$ (X = Cl (**11**), Ph (**12**), OCH_2CF_3 (**13**)). Binuclear complexes $[Cp'_2Zr(X)(\mu\text{-}Cl)M(CO)_4]$ (X = Me, M = Mo, W (**14a,b**), X = O*t*-Bu, M = Mo (**16**)) which contain an additional bridging chloride ligand were obtained similarly from $[M(CO)_4(cycloheptatriene)]$ and the appropriate zirconium compound. The chloride bridge is readily opened by addition of either PMe_3 or *t*-BuNC producing complexes $[Cp'_2ZrCl_2M(CO)_4L]$ (L = PMe_3 (**18a,b**), *t*-BuNC (**19a,b**)) and $[Cp'_2Zr(Cl)(Me)M(CO)_4PMe_3]$ (**20a,b**; M = Mo (**a**), W (**b**)). Exchange of zirconium-bound chloride for organic groups is achieved by treatment of **18a,b** or **19a,b** with LiR which gives $[Cp'_2ZrMe_2M(CO)_4L]$ (L = PMe_3 (**21a,b**), *t*-BuNC (**22a,b**), M = Mo (**a**), W (**b**)) as well as $[Cp'_2ZrR_2Mo(CO)_4PMe_3]$ (R = Ph (**23**), Tol (**24**)). C–C coupling of two nitrile ligands with a Zr-bound methyl group to give a bridging 1,3-diiminato ligand takes place upon reacting Cp'_2ZrMe_2 (**3**) with $[W(CO)_4(NCR)_2]$. The products $[Cp'_2Zr(\mu\text{-}HN{=}C(R){=}CH{=}C(R){=}N)W(CO)_4]$ (R = Ph (**25**), CH_2Ph (**26**)) were fully characterized by magnetic resonance including ^{13}C-NMR of the doubly labelled derivative **26** ′. Protonation of **26** using $[PhMe_2NH]BPh_4$ gives the corresponding 1,3-diimine complex $[Cp'_2Zr(\mu\text{-}HN{=}C(R){-}CH_2{-}C(R){=}N)W(CO)_4]BPh_4$ (R = CH_2Ph, **27**). © 1997 Elsevier Science S.A.

Keywords: Zirconium; Molybdenum; Tungsten; Bimetallic complexes; Ligand coupling

1. Introduction

Complexes in which two metal atoms of very different electron count are held in close proximity seem to offer fascinating opportunities to achieve novel types of reactions as a result of the simultaneous and cooperative interaction of substrate molecules with, e.g., a hard, oxophilic and a soft, carbophilic metal center. In order to preserve the integrity of the binuclear complex it seems advisable to tie the two metal atoms together with bridging ligands [2–11]. Phosphino-substituted cyclopentadienes have proven to be particularly reliable braces to hold a titanium or zirconium atom and a 'late' transition metal in close proximity [12,13]. Additional interest in this field arises from the notion that complexes of this type can be seen as molecular models of metal-oxide supported heterogeneous catalysts [14,15]. Despite these expectations the success in terms of finding true examples of reactions involving both metal centers has remained rather limited.

Some time ago we have reported the synthesis of binuclear complexes which, in addition to two bridging diphenylphosphino–cyclopentadienide ligands, contain a chloride bridge between a d^0 and a d^6 metal center. This bridge is rapidly opened even by weakly coordinating ligands such as acetonitrile (Eq. (1)) [1,12], thus allowing for the facile addition of substrate molecules. Here we report on the extension of this work to com-

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[1] For Part II, see Ref. [1].

[2] Dedicated to Prof. Waldemar Adam on the occasion of his 60th birthday.

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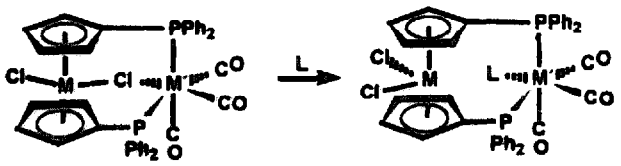
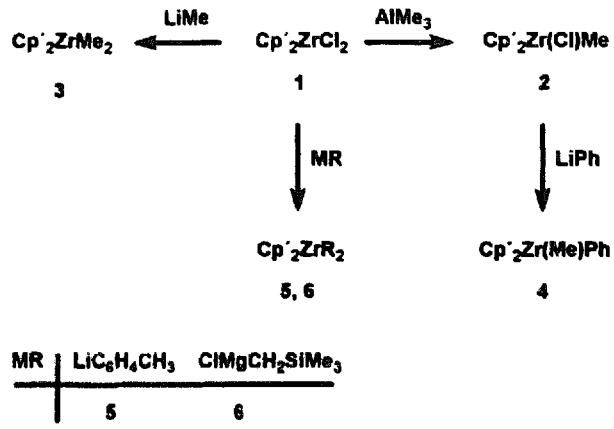
plexes containing zirconium–oxygen and zirconium–carbon bonds.



M = Ti, Zr; M' = Cr, Mo, W

L = MeCN, $P(OMe)_3$, CO (1)



Scheme 1.

2. Results and discussion

2.1. Mononuclear zirconium complexes

The well-known zirconium complexes **1–3** [16,17] (Scheme 1) form the basis of our present work. **2** has been synthesized previously by cleaving a methyl group from **3** with lead dichloride [17]. A more convenient access to **2** is the selective monomethylation [18,19] of **1** using trimethylaluminium. Reaction of **2** with phenyllithium gave the mixed organozirconium complex **4** while the symmetrical complexes **5** and **6** were obtained as usual by treating **1** with the respective lithium or Grignard reagents. **4–6** are colourless crystalline compounds which are soluble without decomposition only in THF or benzene. Their ^{1}H-NMR spectra in the 5–7 ppm region are quite characteristic. The symmetrical compounds **5** and **6** exhibit two narrow multiplets as expected for an AA'MM' spin system, while in the unsymmetrical compound **4** all protons on each Cp' ligand are nonequivalent giving rise to four well-separated multiplet signals (Table 1). This feature turns out to aid greatly in the identification of unknown products.

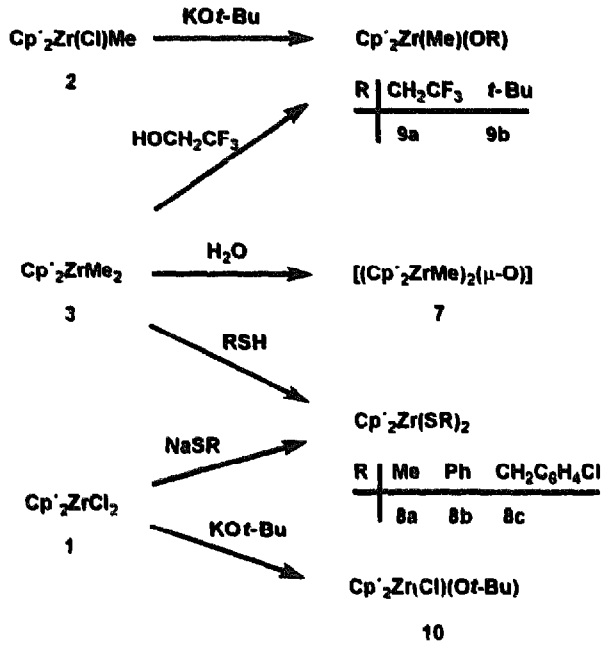
Organozirconium complexes of this type are extremely moisture sensitive. When **3** is taken up in a solvent which has not been rigorously purified, it is immediately transformed into the binuclear oxo-bridged complex **7** which was isolated as an off-white microcrystalline powder. The analogous compound $[(Cp_2ZrMe)_2(\mu\text{-}O)]$ is well-known and has been characterized by X-ray crystallography [19]. This high reactivity towards protic reagents can be exploited for the synthesis of substitution products as shown in Scheme 2.

Thiols rapidly cleave off both methyl groups, the strongly π-donating alkoxide substituent, however, seems to stabilize the unsymmetrical exchange product against further nucleophilic attack. This, of course, aids also in the selective exchange of one chloride ligand as shown by the synthesis of **10**, while with thiolate as a nucleophile only complete substitution is observed (Scheme 2). The spectroscopic properties of complexes **7–10** are similar to those of the diorgano-zirconocenes. Occasionally some of the ^{1}H(Cp')-resonances coincide, e.g., for **8c** (only one broad signal observed) or **9b** (two broad signals in 6:2 intensity ratio). The ^{31}P-resonances

Table 1
NMR spectroscopic data of mononuclear zirconium complexes Cp'_2ZrRR' (**4–10**) [a]

No	R	R'	^{1}H-NMR (C_6D_6) Cp'	R, R'	^{31}P-NMR (C_6D_6)
4	Me	Ph	5.77 5.98 6.14 6.27	0.41	−18.9
5	$(C_6H_4CH_3)_2$		5.95 6.44	2.36 (CH_3)	−18.3
6	$(CH_2SiMe_3)_2$		5.97 6.21	0.33 (CH_2) 0.05 (Me)	−17.9
7	Me	–O–	5.77 5.90 6.14 6.27	0.40	−18.9
8a	$(SMe)_2$		5.87 5.98	2.66 (SMe)	−19.7
8b	$(SPh)_2$		6.02 6.26		−18.1
8c	$(SCH_2C_6H_4Cl)_2$		5.90	4.12 (SCH_2)	−19.8
9a	Me	OCH_2CF_3	5.83 5.92 5.96 6.00	0.43 (Me) 3.88 (OCH_2) [b]	−19.8
9b	Me	O*t*-Bu	5.99 6.34	0.32 (Me) 1.01 (*t*-Bu)	−19.3
10	Cl	O*t*-Bu	6.15 6.27	1.09 (*t*-Bu)	−18.7

[a] Aryl signals in the 6.5–8.0 ppm region are uncharacteristic and have been omitted.
[b] $J(F-H) \approx 9$ Hz.

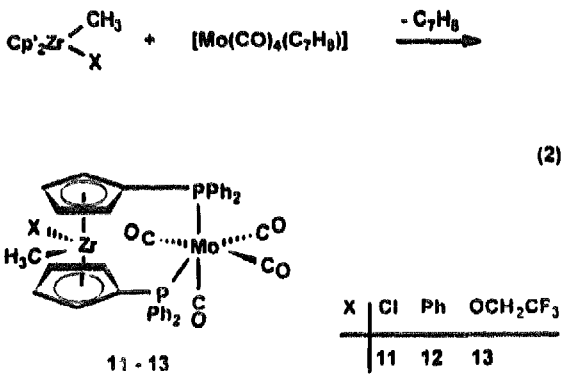


Scheme 2.

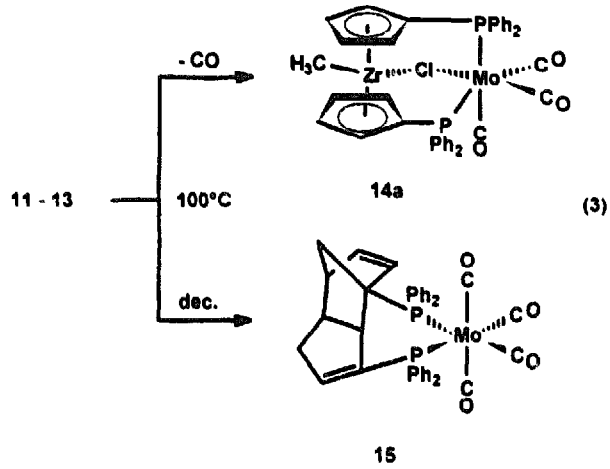
of all compounds appear in the expected range at −17 to −20 ppm.

2.2. Binuclear complexes

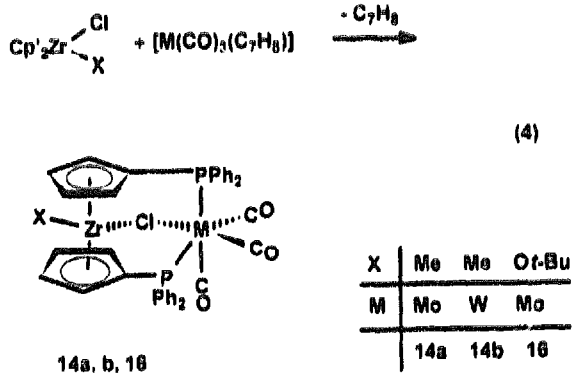
We have shown previously that **1** and **8a** can act as either *bi-* or *tri*-dentate ligands towards carbonyl complexes of the chromium triad [1,12] through donation of electron pairs from both phosphorus atoms as well as the chloride or thiolate group, respectively. Similarly the unsymmetrical methyl zirconocenes **2**, **4**, and **9a** react with tricarbonyl(norbornadiene)molybdenum to give the binuclear complexes **11–13** (Eq. (2)).



These are yellow microcrystalline compounds whose nature is immediately apparent from their spectroscopic data (Table 2). Of note are four different ^{1}H-NMR signals of the inequivalent Cp′ protons and a downfield resonance at ca. 30 ppm for the Mo-coordinated PPh_2 groups. Upon heating in toluene **11** gives off a CO ligand to form the purple Cl-bridged complex **14a** while **12** and **13** decompose into a variety of products of which the mononuclear molybdenum complex **15** [20] could be identified (Eq. (3)). This fairly ready cleavage of the Cp′ ligands from zirconium was quite unexpected and turned out to be a recurring problem in the chemistry of these binuclear systems.



A cleaner access to triply bridged complexes is provided by the reaction of the zirconocene precursors with tricarbonyl(cycloheptatriene) complexes of molybdenum or tungsten (Eq. (4)).



For M = W the reaction is quite slow but can be accelerated by adding a small amount of cobaltocene as an electron transfer catalyst [21]. **14a,b** are deep purple microcrystalline materials while **16** is an orange–brown compound. Despite repeated attempts, we have been unable to grow X-ray quality crystals of any of these triply bridged complexes. In part this is due to the high

sensitivity of these compounds and the limited range of suitable solvents. Spectroscopically, these triply-bridged binuclear complexes are similar to the dichloro derivatives we have reported previously [1,12] (Table 2). A particularly characteristic feature is the additional high-field shift of the ^{31}P resonances brought about by the presence of a third bridge between the two metal atoms. This is certainly a steric effect rather than an electronic one, similar to the 'chelate ring contribution' to the ^{31}P-NMR shift of regular organophosphine ligands [22].

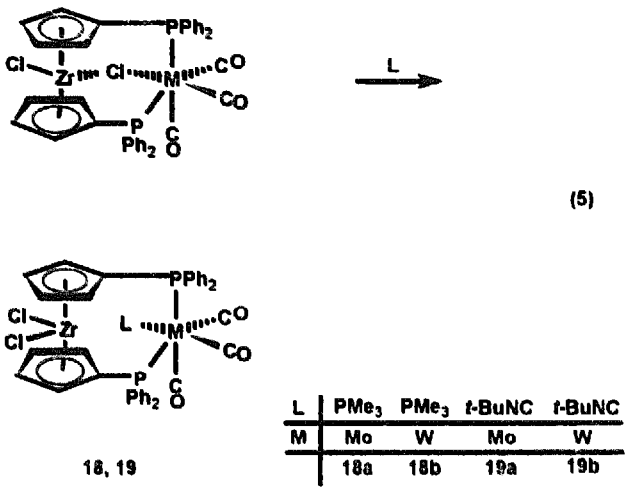
In our previous work we have noted that halide bridges of this type are readily opened by adding small ligand molecules such as MeCN, $P(OMe)_3$, or CO. For comparison, we have treated the complexes **17a,b** [12] with PMe_3 or *t*-BuNC and obtained the expected substitution products **18a,b** and **19a,b** (Eq. (5)).In much the

Table 2
NMR spectroscopic data of binuclear complexes $[Cp'_2Zr(RR')M(CO)_3L]$ (**11–27**) [a]

No	^{1}H-NMR (C_6D_6) Cp'	R,R'	L	^{31}P-NMR (C_6D_6)
11	5.78 5.91 6.33 6.58	0.34 (Me)		31.2
12	5.60 5.99 6.32	0.05 (Me)		30.9
13	5.63 5.82 6.16 6.27	0.28 (Me)		30.2
		3.87 (OCH_3) [b]		
14a	6.05 – 6.48 6.65 6.86	0.50 (Me)		21.0
14b	6.16 6.31 6.64 6.83	0.70 (Me)		9.2
16	6.01 6.11 6.22 6.60	1.18 (*t*-Bu)		26.8
18a	6.38 6.46 6.49		0.61 (PMe_3) [c]	32.8 [d], −27.4 [d]
18b [e]	6.50 6.61 6.75 6.80		0.82 (PMe_3) [f]	16.6 [g], −49.8 [h]
19a [e]	6.51 6.67 6.69		1.08 (*t*-Bu)	33.0
19b	6.35 6.38 6.56 6.71		0.78 (*t*-Bu)	16.7 [i]
20a	6.10–6.90 (m)	0.23 (Me)	0.60 (PMe_3) [j]	31.0 [k], −27.8 [k]
		0.36 (Me)	0.70 (PMe_3) [j]	31.5 [k], −27.2 [k]
20b [e]	6.30–7.00 (m)	0.09 (Me)	0.80 (PMe_3) [c]	15.0 [l], −46.3 [l]
		0.26 (Me)	0.87 (PMe_3) [c]	15.3 [l], −46.3 [l]
21a	6.18 6.38 6.52 6.74	−0.35 (Me)	0.70 (PMe_3) [c]	30.0 [d], −27.5 [d]
		−0.23 (Me)		
21b	6.06 6.30 6.44 6.66	−0.32 (Me)	0.75 (PMe_3) [f]	14.6 [m], −46.5 [m]
		−0.21 (Me)		
22a	6.16 6.23 6.36 6.55	−0.16 (Me)	0.76 (*t*-Bu)	31.7
		−0.18 (Me)		
22b	6.13 6.23 6.38 6.56	−0.12 (Me)	0.74 (*t*-Bu)	14.9 [n]
		−0.15 (Me)		
23	6.35 6.56 6.72		0.80 (PMe_3) [c]	31.5 [d], −27.5 [d]
24	6.40 6.50 6.76	2.12 (Me)	0.77 (PMe_3) [c]	31.3 [k], −27.9 [k]
		2.19 (Me)		
25	5.04 5.46 5.63 5.74	5.40 (NH)	5.73 (CH) [o]	7.5 [p]
26	4.96 5.39 5.46 5.50	2.94 (CH_3)	4.66 (CH_3)	6.0 [q]
		4.74 (NH)	5.10 (CH) [q]	
27	4.71 4.93 5.61 5.79	3.16 (CH_3)	4.30 (CH_3)	10.3 [r]
		8.63 (NH)	3.25 (CH_3)	

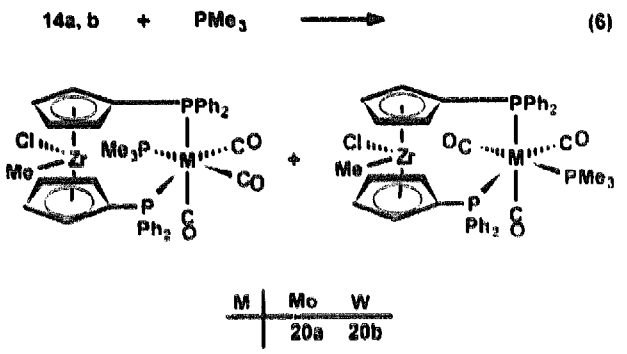
[a] Aryl signals in the 6.5–8.0 ppm region are uncharacteristic and have been omitted.
[b] $^4J(F-H) = 9$ Hz.
[c] $^2J(P-H) = 6$ Hz.
[d] $^2J(P-P) = 26$ Hz.
[e] Recorded in CD_2Cl_2.
[f] $^3J(P-H) = 7$ Hz.
[g] $^1J(W-P) = 234$ Hz, $^2J(P-P) = 25$ Hz.
[h] $^1J(W-P) = 213$ Hz, $^2J(P-P) = 25$ Hz.
[i] $^1J(W-P) = 241$ Hz.
[j] $^2J(P-P) = 27$ Hz.
[k] $^2J(P-P) = 25$ Hz.
[l] $^2J(P-P) = 24$ Hz.
[m] $^1J(W-P) = 237$ Hz.
[n] $^4J(H-H) = 2$ Hz.
[o] $^1J(W-P) = 225$ Hz.
[p] $^4J(H-H) = 1$ Hz.
[q] $^1J(W-P) = 226$ Hz.
[r] $^1J(W-P) = 224$ Hz.

same way the chloride bridge of **14a,b** is opened in the presence of PMe_3 (Eq. (6)).



(5)

L	PMe_3	PMe_3	*t*-BuNC	*t*-BuNC
M	Mo	W	Mo	W
	18a	18b	19a	19b

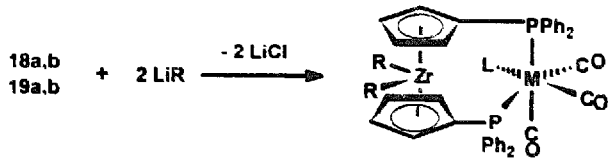


(6)

M	Mo	W
	20a	20b

These reactions are accompanied by a conspicuous colour change from deep purple to yellow. ^{31}P-NMR spectroscopy reveals that **20a,b** are formed as 1:1 mixtures of two diastereoisomers. This indeed had to be expected for a reaction which as a first step involves the dissociation of the M–Cl bond followed by a rapid rearrangement of the five-coordinated intermediate $[M(CO)_3(PPh_2R)_2]$ [23].

The zirconium-bound chloride ligands of **18a,b** and **19a,b** can be exchanged for methyl or aryl groups by treatment with organolithium reagents (Eq. (7)). The new compounds are yellow microcrystalline powders which, like their mononuclear counterparts **3–6**, are highly sensitive towards oxygen, moisture, and halocarbon solvents. NMR spectra could therefore be recorded only in C_6D_6 where these compounds have limited solubility. The most conspicuous feature is the non-equivalence of the diastereotopic methyl groups of **21a,b** and **22a,b**.



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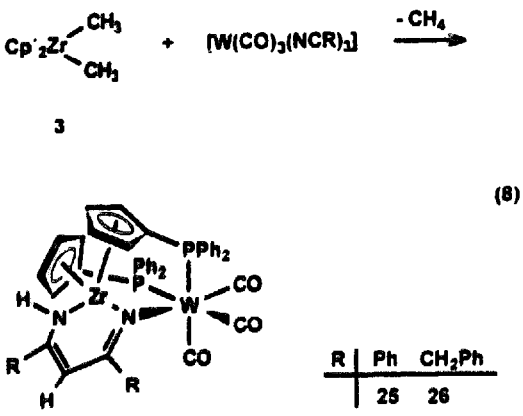
(7)

R	Me	Me	Me	Me	Ph	Tol
L	Me_3P	Me_3P	*t*-BuNC	*t*-BuNC	Me_3P	Me_3P
M	Mo	W	Mo	W	Mo	Mo
	21a	21b	22a	22b	23	24

It was hoped that the high reactivity of the zirconium–carbon σ bonds in combination with the high electron density at the d^0 metal center would give rise to insertion reactions of the metal–coordinated carbon monoxide or isonitrile ligands. Even careful heating in toluene, however, produced only an intractable mixture of decomposition products among which the Cp-dimer derived complex **15** could be identified in some instances. Considerable effort was also made to generate a zirconium cation by cleaving off a methyl group either by oxidation or by treatment with various Brønstedt acids [24], again without any success. Monitoring such reactions by ^{1}H and ^{31}P-NMR indicated extensive decomposition accompanied by carbonyl scrambling. This time, the d^0 metal center appears to be the 'weak spot' of these systems.

In still another attempt at synthesizing binuclear complexes which contain reactive groups at both metal centers, Cp'_2ZrMe_2 (**3**) was treated with the tris(nitrile) complexes $[M(CO)_3(NCR)_3]$ (M = Mo, R = Me; M = W, R = Me, Et). A steady colour change of the solution to deep orange indicated a fairly rapid reaction of the two compounds. NMR monitoring, however, revealed that the expected coupling products analogous to **22** (L = RCN instead of *t*-BuNC) were not formed. The signals of the Zr-bound methyl groups disappeared altogether, only one nitrile molecule per Mo or W complex was liberated, and two widely separated signals for methyl or ethyl groups, respectively, appeared indicating that some transformation of the nitrile ligands had occurred. In addition, a weak signal at ca. 5 ppm hinted at the formation of some kind of an unsaturated system. The remaining spectral data were clean but did not yield any further clues regarding the nature of the new compounds. All attempts at isolation proved fruitless due to an unfortunate combination of high sensitivity and low propensity to crystallize.

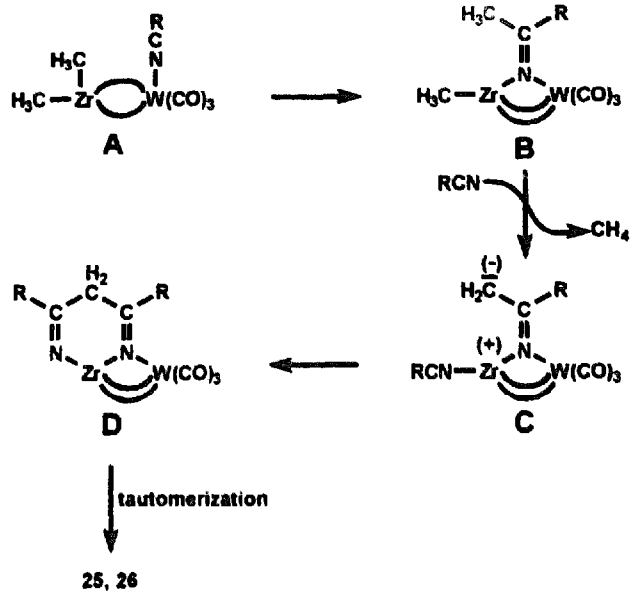
Analogous but readily isolable products were obtained from the reaction of **3** with the tris(benzonitrile) and tris(benzylcyanide) complexes of tungsten (Eq. (8)).



(8)

25 and **26** are maroon microcrystalline solids which are readily soluble in benzene or toluene. In addition to the ^{1}H-NMR signals (Table 2) analogous to those mentioned above a weak broad signal was found which can be assigned to a NH group. The ^{13}C-NMR spectra exhibit two low-field signals at 162 and 184 ppm, the latter split into a narrow triplet due to coupling to two equivalent phosphorus nuclei. An additional signal is found at 106 ppm, a region typical for the central carbon atom of 1,3-diiminato complexes [25]. In order to further corroborate this assignment reaction (8) was repeated using $[W(CO)_3(N^{15}CCH_2Ph)_3]$ (90% enriched). The resulting doubly labelled compound **26*** did indeed show the expected enhancement of the two ^{13}C signals at 162.5 and 183.8 ppm, and no ^{13}C–^{13}C coupling. This allows us to clearly rule out a 1,2-diimine structure which might have been formed by the reductive coupling of two nitrile ligands [26].

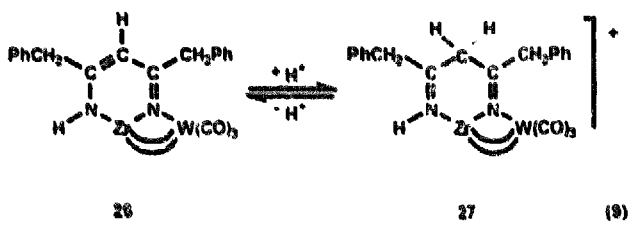
The formation of **25** and **26** must at some stage involve the insertion of the nitrile into the zirconium–carbon bond. It has been noted earlier that neutral complexes Cp_2MR_2 (M = Ti, Zr) do not react with nitriles [27], and this was corroborated also by a control experiment involving **3** and benzyl cyanide. Cationic organozirconocenes, however, do insert the C–N triple bond, the active species being the coordinatively saturated complexes $[Cp_2Zr(R)(NCMe)_2]^+$ [27] which can be obtained from Cp_2ZrR_2 by either protonolysis or oxidation [24] in acetonitrile solvent. One might thus suspect that in the present case a similar intermediate is formed in small amounts by the action of minute traces of acid or oxidants. However, even with pure $[Cp_2Zr(Me)(NCMe)_2]^+$ the insertion is slow (80% completion after 45 h at 23°C [27]) such that the presence of an analogous binuclear cation in trace quantities could not account for the smooth formation of compounds **25** and **26**. We, therefore, consider a different course of events as outlined in Scheme 3 more likely.



Scheme 3.

Promoted by the close proximity of the two metal centers, the initially formed binuclear complex **A** undergoes an intramolecular methyl transfer to the tungsten-coordinated nitrile. A proton is then transferred from the acidic α-methyl group of the imine to the basic metal-bound methyl group. The vacant site thus created at zirconium is taken up by a nitrile molecule which is then attacked by the enolate-type methylene group to give the 1,3-diiminato complex **D**. A somewhat similar mechanism has been proposed for the addition of two anisonitrile molecules to $Cp_2^*ScCH_3$ [28]. Proton migration finally yields the end products **25** and **26**, respectively.

The diimine ligands in **25** and **26** are apparently quite tightly bound. All attempts at liberation from the complex or controlled hydrolysis to give a 1,3-diketonate complex were unsuccessful. However, **26** can cleanly and reversibly be protonated using weak Brønstedt acids (Eq. (9)).



26 27 (9)

The formation of **27** is accompanied by a conspicuous high-frequency shift of the ν(CO) vibrations of the $W(CO)_3$ group. The ^{13}C signal of the enamine carbon is shifted 26 ppm downfield to 188.5 ppm while that of

the bridging imine group experiences a slight upfield shift. The methine signal at 106.0 ppm is replaced by a methylene signal at 57.7 ppm. The protons at this methylene group resonate a 5.32 ppm while the NH proton is shifted even further downfield to 8.63 ppm. Taken together this is convincing evidence that protonation takes place at the central carbon atom of the 1,3-diiminato ligand.

3. Conclusions

Established synthetic methods provide a variety of PPh_2-substituted zirconocene derivatives which are suitable building blocks for the construction of binuclear metal complexes. The presence of a late transition metal in the system does in general not interfere with the usual nucleophilic substitution reactions at zirconium. Ligand addition to the late transition metal is particularly facile for bimetallic complexes which contain a chloride bridge that can be opened under mild conditions. However, true examples of a cooperative action of both metal centers in ligand-based reactions are still rare. More work is obviously required in order to establish a generalized concept of bimetallic activation.

4. Experimental section

All manipulations were carried out in Schlenk-type glassware under an atmosphere of purified nitrogen or argon. Solvents were dried and distilled under nitrogen prior to use. NMR solvents were degassed and stored under nitrogen over molecular sieves. NMR: Bruker AC 200, Bruker AMX 400; chemical shifts are reported in ppm vs. TMS (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). IR: Bruker IFS 25, Perkin-Elmer 283.

The following starting materials were prepared by published procedures: Cp'_2ZrCl_2 (**1**) [16], Cp'_2ZrMe_2 (**3**) [17], [Mo(CO)$_4$(norbornadiene)] [29], [M(CO)$_3$(cycloheptatriene)] (M = Mo, W) [30,31], [ClZr(μ-$C_5H_4PPh_2$)$_2$(μ-Cl)M(CO)$_3$] (M = Mo (**17a**), W (**17b**)) [12], [M(CO)$_3$(NCR)$_3$] (M = Mo, R = Me; M = W, R = Me, Et, Ph) [31,32], $PhCH_2^{13}CN$ [33]. All other reagents were used as obtained commercially.

4.1. $Cp'_2Zr(Cl)Me$ (2)

To a solution of Cp'_2ZrCl_2 (**1**) (1.73 g, 2.61 mmol) in toluene (50 ml) is added at −70°C a solution of $AlMe_3$ in toluene (3.0 ml, 6.0 mmol). After 10 min the mixture is allowed to warm up to room temp. and stirred for 24 h. Then $[Ph_4P]Cl$ (1.03 g, 2.75 mmol) is added, the mixture is stirred again for a few minutes and filtered. The filtrate is concentrated to a few milliliters and the product precipitated by addition of pentane. Yield 1.14 g (68%), slightly yellow crystalline powder. The spectroscopic properties agree with the data given in the literature [17].

4.2. $Cp'_2Zr(Me)Ph$ (4)

To a solution of $Cp'_2Zr(Cl)Me$ (**2**) (0.21 g, 0.33 mmol) in THF (5 ml) is added a solution of PhLi in ether (0.52 mol/l, 0.33 mmol). After 1 h the solvent is removed under vacuum and the residue extracted with benzene. After partial evaporation of the solvent the product is precipitated by adding pentane. Yield 0.17 g (76%), yellow crystalline powder, dec. 110°C. Due to the high air sensitivity of this material satisfactory elemental analyses could not be obtained.

4.3. $Cp'_2Zr(C_6H_4CH_3)_2$ (5)

To a solution of Cp'_2ZrCl_2 (**1**) (0.63 g, 0.96 mmol) in benzene (15 ml) is added a solution of para-tolyllithium in ether (2.0 mmol) and allowed to react for 20 min at 20°C. The solution is then filtered and concentrated, and the product is precipitated by adding pentane. Yield 0.52 g (70%), yellow crystalline powder, m.p. 75°C. Due to the high air sensitivity of this material satisfactory elemental analyses could not be obtained.

4.4. $Cp'_2Zr(CH_2SiMe_3)_2$ (6)

A solution of Cp'_2ZrCl_2 (**1**) (0.98 g, 1.48 mmol) in benzene (25 ml) is treated with an excess of Me_3SiCH_2MgCl (4.0 mmol) in ether at 20°C. After 15 h the mixture is taken to dryness and the residue extracted with pentane. The solution is filtered and concentrated, and the product is allowed to crystallize at −70°C. Yield 0.61 g (54%), yellow crystalline powder, dec. 85°C. Anal. found: C, 67.18; H, 6.56. $C_{42}H_{50}P_2Si_2Zr$ (764.20) calc.: C, 66.01; H, 6.60.

4.5. $[(Cp'_2ZrMe)_2(\mu\text{-}O)]$ (7)

Cp'_2ZrMe_2 (**3**) (0.50 g, 0.81 mmol) is dissolved in untreated THF (15 ml) and allowed to stand for 30 min. The solution is concentrated and filtered, and the product precipitated by adding pentane. Yield 0.30 g (60%), off-white powder, m.p. 140°C (dec.). Anal. found: C, 67.57; H, 4.83. $C_{70}H_{62}OP_4Zr_2$ (1225.60) calc.: C, 68.60; H, 5.10.

4.6. $Cp'_2Zr(SMe)_2$ (8a), $Cp'_2Zr(SPh)_2$ (8b)

To a solution of Cp'_2ZrCl_2 (**1**) (0.56 g, 0.85 mmol) in THF (15 ml) is added a slight excess (1.85 mmol) of the respective sodium thiolate. The mixture is stirred for 3 h, evaporated, and extracted with benzene. After filtration the product is crystallized by adding pentane.

8a: Yield 0.37 g (64%), orange crystalline powder, m.p. 110°C (dec.). Anal. found: C, 63.62; H, 5.51. $C_{36}H_{34}P_2S_2Zr$ (683.96) calc.: C, 63.22; H, 5.01.

8b: Yield 0.57 g (83%), orange crystalline powder, m.p. 97°C (dec.). Anal. found: C, 66.73; H, 4.57. $C_{46}H_{38}P_2S_2Zr$ (808.11) calc.: C, 68.37; H, 4.74.

4.7. $Cp'_2Zr(SCH_2C_6H_4Cl)_2$ (8c)

To a solution of Cp'_2ZrMe_2 (3) (0.26 g, 0.42 mmol) in ether (5 ml) is added para-chlorobenzyl thiol (0.16 g, 1.01 mmol). After 2 d the solution is concentrated and the product precipitated by addition of pentane. Yield 0.29 g (81%), orange crystalline powder, m.p. 121°C. Anal. found: C, 64.64; H, 4.57. $C_{48}H_{40}Cl_2P_2S_2Zr$ (905.05) calc.: C, 63.70; H, 4.46.

4.8. $Cp'_2Zr(Me)OCH_2CF_3$ (9a)

To a solution of Cp'_2ZrMe_2 (3) (0.11 g, 0. 18 mmol) in THF (5 ml) a stoichiometric amount of 2,2,2-trifluoroethanol (13 μL) is added. Further workup as described above for **8c** gave **9a** as a beige microcrystalline powder. Yield 0.07 g (62%), dec. 96°C. Anal. found: C, 63.89; H, 4.62. $C_{37}H_{33}F_3OP_2Zr$ (703.83) calc.: C, 63.14; H, 4.73.

4.9. $Cp'_2Zr(Me)O(t\text{-}Bu)$ (9b)

To a solution of $Cp'_2Zr(Cl)Me$ (2) (0.41 g, 0.64 mmol) in THF (10 ml) an excess of KO*t*-Bu (0.15 g, 1.33 mmol) is added. After stirring for one hour the solvent is removed and the residue extracted twice with 10 ml of benzene. The filtered extract is concentrated and the product precipitated with pentane. Yield 0.34 g (78%), yellow crystalline powder, dec. 112°C. Anal. found: C, 68.68; H, 5.75. $C_{39}H_{40}OP_2Zr$ (677.92) calc.: C, 69.10; H, 5.95.

4.10. $Cp'_2Zr(Cl)O(t\text{-}Bu)$ (10)

A solution of Cp'_2ZrCl_2 (1) (0.42 g, 0.64 mmol) in THF (10 ml) is treated as described above for **9b**. Yield 0.32 g (78%), yellow crystalline powder, dec. 112°C. Anal. found: C, 65.45; H, 5.86. $C_{38}H_{37}ClOP_2Zr$ (698.33) calc.: C, 65.36; H, 5.34.

4.11. $[Cp'_2Zr(Me)(X)Mo(CO)_4]$, X = Cl (11), Ph (12), OCH_2CF_3 (13)

The mononuclear zirconium complex $Cp'_2Zr(Me)X$ (0.45 mmol) is taken up in 10 ml of either dichloromethane (X = Cl, OCH_2CF_3) or benzene (X = Ph). After adding $[Mo(CO)_4(norbornadiene)]$ (0.15 g, 0.50 mmol) the mixture is stirred for 30 min. The volume of the solution is then reduced to a few milliliters and the product precipitated by adding pentane. The solid is filtered off, washed repeatedly with pentane, and dried.

11: Yield 0.34 g (88%), yellow crystals, m.p. 128°C (dec.). IR (Nujol): 2014(m), 1929(s), 1904(vs), 1883(s) cm^{-1} (CO). Anal. found: C, 55.09; H, 3.94. $C_{39}H_{31}ClMoO_4P_2Zr$ (848.23) calc.: C, 55.22; H, 3.68.

12: Yield 0.32 g (79%), yellow crystals, m.p. 113°C. Anal. found: C, 60.62; H, 4.36. $C_{45}H_{36}MoO_4P_2Zr$ (889.89) calc.: C, 60.74; H, 4.08.

13: Yield 0.31 g (76%), yellow crystalline powder, m.p. 97°C. IR (Nujol): 2017(m), 1927(s), 1898(vs) cm^{-1} (CO). Anal. found: C, 54.30; H, 3.85. $C_{41}H_{33}F_3MoO_5P_2Zr$ (911.81) calc.: C, 54.01; H, 3.65.

4.12. $[Cp'_2Zr(X)(\mu\text{-}Cl)M(CO)_5]$, X = Me, M = Mo (14a), M = W (14b), X = O(*t*-Bu), M = W (16)

The mononuclear zirconium complex $Cp'_2Zr(X)Cl$ (0.59 mmol) is taken up in benzene (10 ml). After addition of $[M(CO)_3(cycloheptatriene)]$ (0.59 mmol) and a trace of cobaltocene for M = W the mixture is stirred for 45 min and worked up as described above for **11–13**.

14a: Yield 0.37 g (76%), purple crystalline powder, m.p. 142°C (dec.). IR (Nujol): 1940(s), 1855(s), 1822(s) cm^{-1} (CO). Anal. found: C, 55.50; H, 4.06. $C_{38}H_{31}ClMoO_5P_2Zr$ (820.22) calc.: C, 55.65; H, 3.81.

14b: Yield 0.39 g (73%), purple crystals, m.p. 127°C. IR (Nujol): 1938(s), 1854(s), 1827(s) cm^{-1} (CO). Anal. found: C, 50.70; H, 4.03. $C_{38}H_{31}ClO_5P_2WZr$ (908.13) calc.: C, 50.26; H, 3.44.

16: Yield 0.33 g (64%), orange–brown crystalline powder, m.p. 127°C. IR (Nujol): 1939(s), 1848(s), 1807(s) cm^{-1} (CO). Anal. found: C, 56.03; H, 4.64. $C_{41}H_{47}ClMoO_4P_2Zr$ (878.30) calc.: C, 56.07; H, 4.25.

4.13. $[Cp'_2ZrCl_2M(CO)_4L]$, L = PMe_3, M = Mo (18a), W (18b), L = *t*-BuNC, M = Mo (19a), W (19b)

To a solution of the binuclear complex **17a,b** (0.80 mmol) in dichloromethane (10 ml) is added a slight excess (0.90 mmol) of trimethylphosphine or tert.-butyl isonitrile. After the mixture has been stirred for 30 min it is worked up as described above for **11–13**.

18a: Yield 0.61 g (83%), yellow crystals, m.p. 150°C (dec.). IR (CH_2Cl_2): 1943(s), 1853(s), 1835(s) cm^{-1} (CO). Anal. found: C, 52.75; H, 4.26. $C_{40}H_{37}Cl_2MoO_4P_3Zr$ (916.72) calc.: C, 52.41; H, 4.07.

18b: Yield 0.61 g (76%), yellow crystals, m.p. 210°C (dec.). IR (CH_2Cl_2): 1940(s), 1845(s), 1825(s) cm^{-1} (CO). Anal. found: C, 47.37; H, 4.19. $C_{40}H_{37}Cl_2O_4P_3WZr$ (1004.63) calc.: C, 47.82; H 3.71.

19a: Yield 0.58 g (79%), yellow crystalline powder, dec. 165°C. IR (Nujol): 2119(s) cm^{-1} (CN); 1936(s), 1858(s), 1840(s) cm^{-1} (CO). Anal. found: C, 54.19; H,

4.05; N, 1.41. $C_{42}H_{37}Cl_2MoNO_3P_2Zr$ (923.77) calc.: C, 54.61; H, 4.04; N, 1.52.

19b: Yield 0.43 g (53%), yellow crystalline powder, m.p. 160°C (dec.). IR (CH_2Cl_2): 2115(s) cm^{-1} (CN); 1939(s), 1857(s), 1847(s) cm^{-1} (CO). Anal. found: C, 50.23; H 3.71; N, 0.97. $C_{42}H_{37}Cl_2NO_3P_2WZr$ (1011.69) calc.: C, 49.86; H, 3.69; N 1.38.

4.14. [$Cp'_2Zr(Me)ClM(CO)_3(PMe_3)$], M = Mo (20a), W (20b)

A solution of the binuclear complex **14a,b** (0.50 mmol) in benzene (10 ml) is treated with a slight excess (0.60 mmol) of trimethylphosphine for 1 h. Workup as described above for **11–13**. **20a**: Yield 0.34 g (76%), yellow crystalline powder, m.p. 158°C (dec.). IR (Nujol): 1935(s), 1850(s), 1827(s) cm^{-1} (CO). Anal. found: C, 55.20; H, 4.61. $C_{41}H_{40}ClMoO_3P_3Zr$ (896.30) calc.: C, 54.94; H, 4.50.

20b: Yield 0.33 g (68%), yellow crystals, m.p. 153°C. IR (Nujol): 1930(s), 1840(s), 1823(s) cm^{-1} (CO). Anal. found: C, 49.49; H, 4.22. $C_{41}H_{40}ClO_3P_3WZr$ (984.21) calc.: C, 50.04; H 4.10.

4.15. [$Cp'_2ZrMe_2M(CO)_3(PMe_3)$], M = Mo (21a), W (21b)

To a suspension of the binuclear complex **18a,b** (0.80 mmol) in benzene (20 ml) an exactly stoichiometric amount of methyllithium in ether is added. The mixture is stirred for 30 min at room temperature and then taken to dryness. The residue is extracted with three 10 ml portions of benzene, the combined extracts are evaporated and the product precipitated by adding pentane. **21a**: Yield 0.44 g (62%), yellow crystalline powder, m.p. 160°C (dec.). IR (CH_2Cl_2): 1938(s), 1840(s), 1825(s) cm^{-1} (CO). Anal. found: C, 56.94; H, 4.55. $C_{42}H_{41}MoO_3P_3Zr$ (875.89) calc.: C, 57.59; H, 4.95.

21b: Yield 0.55 g (71%), yellow crystalline powder, m.p. 205°C (dec). IR (Nujol): 1935(s), 1838(s), 1820(s) cm^{-1} (CO). Anal. found: C, 52.50; H, 4.40. $C_{42}H_{41}O_3P_3WZr$ (963.79) calc.: C, 52.34; H 4.50.

4.16. [$Cp'_2ZrMe_2M(CO)_3CN(t\text{-}Bu)$], M = Mo (22a), W (22b)

A suspension of the binuclear complex **19a,b** (0.80 mmol) in benzene (20 ml) is treated with methyllithium and worked up as described above.

22a: Yield 0.57 g (81%), yellow crystalline powder, m.p. 180°C (dec). IR (Nujol): 2123(s) cm^{-1} (CN); 1934(s), 1849(s), 1840(s) cm^{-1} (CO). Anal. found: C, 56.19; H, 4.88; N, 1.52. $C_{44}H_{43}MoNO_3P_2Zr$ (882.94) calc.: C, 59.86; H, 4.91; N, 1.59.

22b: Yield 0.52 g (67%), yellow crystalline powder, m.p. 200°C (dec.). IR (Nujol): 2118(s) cm^{-1} (CN); 1938(s), 1850(s), 1840(s) cm^{-1} (CO). Anal. found: C, 54.50; H, 4.51; N, 1.38. $C_{44}H_{43}NO_3P_2WZr$ (970.85) calc.: C, 54.44; H, 4.46; N 1.44.

4.17. [$Cp'_2ZrR_2Mo(CO)_3(PMe_3)$], R = Ph (23), p-$C_6H_4CH_3$ (24)

A suspension of the binuclear complex **18a,b** (0.80 mmol) in benzene (20 ml) is treated with the respective aryllithium reagent and worked up as described above.

23: Yield 0.46 g (58%), yellow crystalline powder, m.p. 130°C (dec.). IR (THF): 1942(s), 1851(s), 1839(s) cm^{-1} (CO). Anal. found: C, 62.29; H, 5.15. $C_{52}H_{47}MoO_3P_3Zr$ (1000.03) calc.: C, 62.46; H, 4.74.

24: Yield 0.58 g (71%), yellow crystalline powder, m.p. 110°C. IR (THF): 1941(s), 1852(s), 1838(s) cm^{-1} (CO). Anal. found: C, 63.45; H, 5.28. $C_{54}H_{51}MoO_3P_3Zr$ (1028.08) calc.: C, 63.09; H 5.00.

4.18. [$Cp'_2Zr(\mu\text{-}HN\text{-}C(R)=CH\text{-}C(R)=N)W(CO)_3$], R = Ph (25), CH_2Ph (26)

A solution of [$W(CO)_3(NCEt)_3$] (1.00 g, 2.31 mmol) and either benzonitrile (4.00 g, 38.8 mmol) or benzylcyanide (4.00 g, 32.4 mmol) in THF (20 ml) is refluxed for 3 h. The solution is then concentrated, ether is added, and the resulting yellow crystalline powder is filtered off, washed repeatedly with ether, and dried. The product is sufficiently pure (by IR) for the next step. Cp'_2ZrMe_2 (**3**) (0.59 g, 0.96 mmol) and [$W(CO)_3(NCR)_3$] (1.05 mmol) are suspended in benzene and stirred for 18 h at room temperature. The mixture is then filtered, the solution concentrated, and the product precipitated by adding pentane.

25: Yield 0.77 g (74%), maroon crystalline powder, m.p. 116°C. IR (CH_2Cl_2): 1928(s), 1860(s), 1820(s) cm^{-1} (CO). ^{13}C-NMR (THF/acetone-d_6) (selected signals): δ 105.7 (s, *C*H), 161.0 (s, HN*C*Ph), 183.7 (t, ^3J(P–C) = 2 Hz, N=*C*Ph). Anal. found: C, 57.18; H, 3.71; N, 2.79. $C_{52}H_{40}N_2O_3P_2WZr$ (1077.92) calc.: C, 57.94; H, 3.74; N, 2.60.

26: Yield 0.75 g (71%), maroon crystalline powder, m.p. 98°C (dec.). IR (Nujol): 1928(s), 1860(s), 1820(s) cm^{-1} (CO). ^{13}C-NMR (THF/acetone-d_6) (selected signals): δ 45.7 (s, *C*H_2Ph), 56.9 (s, *C*H_2Ph), 106.0 (s, *C*H), 162.5 (s, HN*C*CH_2Ph), 183.8 (t, ^3J(P–C) = 2 Hz, N=*C*CH_2Ph). Anal. found: C, 59.90; H, 4.36; N, 2.42. $C_{54}H_{44}N_2O_3P_2WZr$ (1105.98) calc.: C, 58.64; H, 4.01; N 2.53.

4.19. [$Cp'_2Zr(\mu\text{-}HN\text{-}C^*(CH_2Ph)=CH\text{-}C^*(CH_2Ph)=N)W(CO)_3$] (26*)

The isotopically labeled compound was obtained in the same way on an appropriately reduced (0.40 mmol)

scale. The ^{13}C-NMR spectrum showed a drastic enhancement of the signals at 162.5 and 183.8 ppm.

4.20. $[Cp'_2Zr(\mu\text{-}HN=C(CH_2Ph)-CH_2-C(CH_2Ph)=N)W(CO)_5]BPh_4$ (27)

A solution of **26** (0.50 g, 0.45 mmol) and $[PhMe_2NH]BPh_4$ (0.19 g, 0.43 mmol) in THF (10 ml) was stirred overnight. The mixture was then filtered, partly evaporated, and the product precipitated by adding benzene. Yield 0.56 g (92%), red crystalline powder, m.p. 106°C (dec.). IR (Nujol): 1960(s), 1896(s), 1860(s) cm^{-1} (CO). ^{13}C-NMR (CD_2Cl_2) (selected signals): δ 46.5 (s, CH_2Ph), 47.0 (s, CH_2Ph), 57.7 (s, CH_2), 188.5 (s, $HNCCH_2Ph$), 183.1 (t, $^3J(P-C)=3$ Hz, $N=CCH_2Ph$). Anal. found: C, 63.99; H, 5.34; N, 1.64. $C_{76}H_{65}BN_2O_3P_2WZr$ (1426.22) calc.: C, 65.69; H, 4.59; N 1.96.

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